Quantum Transport in Molecular Rings and Chains

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Abstract

We study charge transport driven by deformations in molecular rings and chains. Level crossings and the associated Longuet-Higgins phase play a central role in this theory. In molecular rings a vanishing cycle of shears pinching a gap closure leads, generically, to *diverging* charge transport around the ring. We call such behavior homeopathic. In an infinite chain such a cycle leads to *integral* charge transport which is independent of the strength of deformation. In the Jahn-Teller model of a planar molecular ring, X_p, there is a distinguished cycle in the space of uniform shears which keeps the molecule in its manifold of ground states and pinches level crossing. The charge transport in this cycle gives information on the derivative of the hopping amplitudes.

1 Introduction

Adiabatic transport describes the nondissipating response of systems driven by time dependence [Avron 1995, Kohmoto 1985, Kunz 1993, Niu 1991, Seiler 1991, Thouless 1994]. An attractive feature of this theory is the geometrization of linear response theory. Its central result is the identification of transport coefficients with components of the adiabatic curvature. Because the theory describes reactive–rather than dissipative–transport, intuition that comes from dissipative (ohmic) transport is of no real value. For example, it allows for charge transport in materials that are nominally insulators [Niu 1994]. The classical counterpart of the theory was studied in [Berry and Robbins 1993].

The focus of our study will be the role of points of gap closures. This is where one expects interesting things to happen. This is also where one can expect to find universal behavior which is, to a large extent, system independent. The basic questions we shall ask is: What distinguishes a cycle that pinches a gap closure from a cycle that does not?

The answer to this question turns out to be related to a question asked by Longuet-Higgins [Longuet-Higgins 1975]: Can one tell if a cycle of Hamiltonians traps a point of level crossing? The answer to Longuet-Higgins question is provided by looking at what is now known as Berry's phase [Berry 1984, Simon 1983]. In the special case of Hamiltonians invariant under time reversal, the phase is ± 1 and is known as the Longuet-Higgins phase. A Longuet-Higgins phase of -1 is associated with conic (aka generic) level crossing, and no crossing has phase 1. The Longuet-Higgins phase has observable implications to the vibrational and rotational spectra of molecules [Mead 1992, Mead and Truhlar 1979, Delacrétaz et al. 1986, Whetten et al. 1986]. What we add to this is that this phase also has observable implication for electronic transport. When the cycle of deformation does not trap a gap closure (so Longuet-Higgins phase is 1), the charge transport is proportional to the *area* of the cycle. The response to weak driving is small. In contrast, a cycle that traps a generic level crossing, with Longuet-Higgins phase -1, is characterized by homeopathic response, where the charge transport in a molecular ring is *inversely* proportional to the length of the cycle. In particular, a vanishing cause leads to a diverging response. In the case of infinite chains the behavior is somewhat different and in some ways more intriguing. It is still true that there is a weak response for a tiny cause when the cycle does not trap a gap closure. But, for a cycle that traps a gap closure, the charge transport is *integral*, independent of the strength of the driving.

Charge pumps are quantum systems where quantized charge transport is driven by a periodic modulation [Niu 1990, Thouless 1983], and have been recently realized [Shilton et al. 1996]. The Thouless-Niu pumps are non-homeopathic: once the driving becomes weak the charge transport drops discontinuously to zero.

Charge transport driven by deformations may be thought of as a generalized version of piezoelectricity. Piezoelectricity was put in a geometric framework in [Resta 1994, King-Smith and Vanderbilt 1993]. In this case, one replaces the global

question — what is the charge transport by a full cycle of deformation — by the local question: What is the ratio of current to the rate of deformation. Diverging piezoelectricity in Hubbard models of perovskites near gap closures was found in numerical studies in [Resta and Sorella 1995]. As we shall explain, near a generic crossing the ratio of current to rate of deformation is inversely proportional to the distance from the crossing in an infinite chain and inversely proportional to the square of the distance in a molecular ring.

The divergence of transport near gap closures has a geometric interpretation. It is an analog of an elementary fact about the curvature of surfaces such as spheres and tori. The average (Gaussian) curvature $\langle\Omega\rangle$ of a surface with g handles, whose area is ε^2 is, by Gauss-Bonnet,

$$\langle\Omega\rangle = \frac{4\pi\,(1-g)}{\varepsilon^2}.$$

The homeopathic behavior of transport is basically the divergence of the (average) curvature as the area, ε^2, shrinks to zero. ε is a measure of the distance from the point of level crossing. In molecular rings the ratio of current to rate of deformation is analogous to the Gaussian curvature and diverges like ε^{-2}. The charge transport in a cycle pinching a gap closure behaves like a line integral of the curvature and is of the order of $1/\varepsilon$.

In the case of infinite chains with infinitely many electrons there is an extra integration over the occupied states in the Brillouin zone. As a consequence, the ratio of current to rate of deformation behaves like a line integral of the curvature and diverges like $1/\varepsilon$. The charge transport in a cycle of deformation is then like an area integral of the curvature. For a g handle surface this gives $2(1-g)$, independent of its area. The corresponding statement for charge transport is that a cycle of deformations transports an integer charge independent of the size of the deformations (provided it encircles the point of gap closure). A model for a charge pump that transports integral charge for infinitesimal cycles is the insulating infinite helix described in section 8.

Quantum charge transport driven by deformation has a classical analog in the theory of elasticity. $SL(2,\mathbb{R})$, the group of uniform shears and rotations of $\mathbb{R}^2$, is generated by

$$g_0 = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \quad g_1 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad g_2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{1}$$

g_1 and g_2 generate shears, and g_0 generates rotations. Since

$$[g_1, g_2] = 2g_0,$$

the commutators of infinitesimal shears generate rigid rotation. Taking an elastic body through a *small* cycle of shears results in an overall rigid rotation. This is, perhaps, the most elementary mechanical analog which mimics the ability of cats to land on their feet by rotating while in free fall [Shapere and Wilczek 1989b,

Purcell 1977]. Using shears to rotate is inefficient: a cycle of deformation of size ε gives a rotation by an angle of order ε^2. The charge transported in such a cycle is also of order ε^2 if the cycle does not pinch gap closure. If it does, the charge is of order $1/\varepsilon$. There appears to be no classical analog of this.

A hallmark of the kind of adiabatic response discussed here is that a molecular quantum system can act as an ac to dc converter. For example, if one drives a cyclic deformation of the molecule by, say, circularly polarized radiation, the response will be a dc current that would give rise to a dc magnetic field. It was established [Cohen-Tannoudji et al. 1969] that nuclei, in his case ^{3}He, can also respond with a dc magnetic field to polarized radiation; in this case this was achieved by biasing the population of up and down spins. The piezoelectric response of molecular rings leads to the same effect by a very different mechanism.

2 An Operator Identity

In this section we derive the basic identity of adiabatic transport which relates the transport coefficients with the components of the adiabatic curvature. This identity is not new [Avron 1995, Bellissard, van Elst and Schulz-Baldes 1994, Kohmoto 1985, Kunz 1993, Niu 1991, Seiler 1991, Thouless 1994]. The purpose of this section is to present it as a consequence of an apparently new operator identity.

Let $H = H(x, \phi)$ be a family of self adjoint Hamiltonians that depend on two parameters x and ϕ. x will stand for a deformation of the molecule and ϕ for a magnetic flux that threads a molecular ring.

$P = P(x, \phi)$ is a spectral projection for H, i.e. $PH = HP$, with $P^2 = P$. Suppose that P is finite dimensional and smooth. This is the case, in particular, if $H(x, \phi)$ is a finite dimensional matrix, as in the examples we consider. The parameter x is slowly evolving in time in a compact interval, i.e. $x(t/\tau)$ such that $\dot{x}(s) = 0$ for $s < 0$ and $s > 1$, see fig. 1. τ is the time scale and the adiabatic limit is $\tau \to \infty$. We shall call $s = t/\tau$ scaled-time, and denote by dot derivatives with respect to s. The quantum evolution is described by a unitary $U = U(s, \phi)$ solving

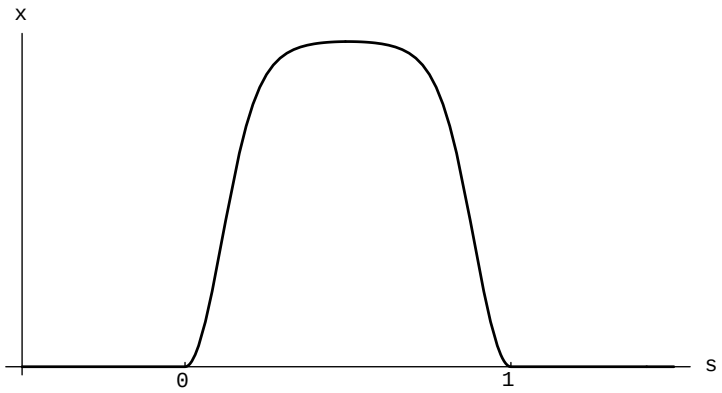

Figure 1: An adiabatic switching of deformation

the initial value problem

$$i\hbar\,\dot{U} = \tau\, H\Big(x(s),\phi\Big)U, \quad U(0,\phi) = 1. \tag{2}$$

Let $P_0 = P_0(\phi)$ denote a spectral projection for $H\Big(x(0),\phi\Big)$. $\rho = \rho(s,\phi) = UP_0U^*$ describes the physical evolution of this projection. ρ is always a projection, but it is a spectral projection only if H is time independent. Since we shall consider Hamiltonians that depend on time, ρ is not a spectral projection in general.

The central identity of adiabatic transport says that

$$\tau\, Tr\Big(\rho\,\partial_\phi H\Big) = \tau\,\partial_\phi\, Tr(PH) + \hbar\, Tr\Big(\Omega_{\phi x}(P)\Big)\,\dot{x} + O\left(\frac{1}{\varepsilon\tau}\right), \tag{3}$$

where

$$\Omega_{\phi x}(P) = -i\,P\,[\partial_\phi P, \partial_x P]\,P, \tag{4}$$

is the ϕx component of the *adiabatic curvature*. In the time independent case, $\dot{x} = 0$, this equation reduces to the Feynman-Hellmann identity. In the time dependent case Eq.(3) says that the expectation value of the observable $\partial_\phi H$ at time t (in a state that solves the time dependent Schrödinger equation and starts as an eigenstate) is made of two parts: A *persistent response* $\partial_\phi Tr(PH)$ that survives in the $\varepsilon\tau \to \infty$ limit, and a *linear response* which is proportional to the rate of deformation $\dot{x}$. The persistent response is leading in the adiabatic expansion (it is of order zero) while the linear response is of order $1/\tau$. In the applications we consider $\partial_\phi H$ is the current operator and $\dot{x}$ is a rate of deformation. The adiabatic curvature $\Omega_{\phi x}(P)$ gives, in this case, the linear dependence of the current on the rate of deformation.

This identity follows from an *operator identity*. For the sake of simplicity we formulate it under stronger conditions than necessary:

Proposition 2.1 *Let P be a spectral projection with smooth parametrical dependence on x and ϕ, for a bounded self-adjoint H, so that P is separated by a gap of size larger than ε from the rest of the spectrum. Let U be the solution of the initial value problem, Eq. (2), and $\rho(s,\phi) = U(s,\phi)P_0(\phi)U^*(s,\phi)$ with P_0 the spectral projection at the initial time. Then, the following operator identity holds (for all times s):*

$$\tau\,\rho\,(\partial_\phi H)\,\rho = \tau\, P(\partial_\phi H)P + \hbar\,\Omega_{\phi x}(P)\,\dot{x} + O\left(\frac{1}{\varepsilon\tau}\right). \tag{5}$$

The point of this identity, Eq (5), is that the left hand side requires the solution of an initial value problem while the right hand side is determined by spectral information alone.

Following [Kato 1958] and [Avron, Seiler and Yaffe 1987], one introduces an auxiliary evolution, $U_A = U_A(s,\phi)$, which respects the spectral splitting with no error. Respecting spectral splitting means that $U_AP_0 = PU_A$. A generator of such an evolution is:

$$\tau\, H_A = \tau\, H + i\hbar\,[\dot{P}, P]. \tag{6}$$

U_A solves the initial value problem:

$$i\hbar\,\dot{U}_A = \tau\, H_A\Big(x(s),\phi\Big)U_A, \quad U_A(0,\phi) = 1.$$

The evolution U_A completely suppresses tunneling between the spectral subspace P and its orthogonal complement. The adiabatic theorem says that U_A stays close to U:

$$U_A = U + O(1/\varepsilon\tau), \quad U^*\partial_\phi U = U_A^*\partial_\phi U_A + O(1/\varepsilon\tau). \tag{7}$$

The adiabatic limit is $\tau\varepsilon \to \infty$. A sufficient condition for the adiabatic theorem to hold is that $\dot{P}$ is smooth and the spectral gap, ε, associated with P does not close. For precise statements and stronger results see [Klein and Seiler 1989, Kato 1958, Nenciu 1993].

From the equation of motion and the chain rule we get:

$$\tau\, U^*\,(\partial_\phi H)\,U = i\hbar\,\Big(U^*\dot{\partial_\phi U}\Big). \tag{8}$$

This identity allows us to compute transport to order τ^{-1} with error terms (which we do not compute) of order τ^{-2} while using the adiabatic theorem to lowest order, Eq. (7). Applying Eq. (8) to the generator of adiabatic evolution gives:

$$\begin{aligned} i\hbar\, U_A P_0\,\Big(U_A^*\dot{\partial_\phi U_A}\Big)\,P_0 U_A^* &= \tau P\,\Big(\partial_\phi H_A\Big)P = \\ \tau P(\partial_\phi H)P + i\hbar P\,[\dot{P},\partial_\phi P]\,P &= \tau\, P(\partial_\phi H)P + \hbar\,\Omega_{\phi x}(P)\,\dot{x}. \end{aligned} \tag{9}$$

From Eq. (8), and the adiabatic theorem:

$$\begin{aligned} \tau\,\rho\,(\partial_\phi H)\,\rho &= \tau\,\Big(UP_0\,U^*\Big)\,(\partial_\phi H)\,\Big(U\,P_0U^*\Big) = \\ i\hbar\,UP_0\,\Big(U^*\dot{\partial_\phi U}\Big)\,P_0U^* &= i\hbar\,U_AP_0\,\Big(U_A^*\dot{\partial_\phi U_A}\Big)\,P_0U_A^* + O\left(\frac{1}{\varepsilon\tau}\right) \\ &= \tau\,P(\partial_\phi H)P + \hbar\,\Omega_{\phi x}(P)\,\dot{x} + O\left(\frac{1}{\varepsilon\tau}\right). \end{aligned}$$

We used the adiabatic theorem in the third step. The other steps are identities. This completes the proof of the operator identity. □

Tracing Eq. (5) gives:

$$\tau\, Tr\,\Big(\rho\,\partial_\phi H\Big) = \tau\, Tr(P\partial_\phi H) + \hbar\, Tr\Big(\Omega_{\phi x}(P)\Big)\,\dot{x} + O\left(\frac{1}{\varepsilon\tau}\right). \tag{10}$$

Since $P\dot{P}P = 0$,

$$\begin{aligned} Tr(\partial P)H &= TrP_\perp(\partial P)PH + TrP(\partial P)P_\perp H \\ &= TrPP_\perp(\partial P)H + Tr(\partial P)P_\perp PH = 0, \end{aligned}$$

where $P_\perp = 1 - P$ is the orthogonal projection on the complement of P. This gives Eq. (3).

In the adiabatic limit the persistent response dominates except in the case where $\partial_\phi Tr(PH) = 0$. In this case the response in the adiabatic limit is governed by the adiabatic curvature. This is the case we are interested in.

There are two mechanisms that make the persistent response vanish:

1. Time Reversal: Suppose that $H(x,0)$ is time reversal invariant and that $\Big(\partial_\phi H\Big)(x,0)$ is odd under time reversal. Then, an elementary argument shows that $\partial_\phi Tr(PH)(x,0) = 0$. There are no persistent currents in deformed molecules in the absence of external magnetic field, and provided time reversal is not spontaneously broken.

2. Unitary Families: In the case that the ϕ dependence of the Hamiltonian comes from a unitary transformation, i.e.

$$H(x,\phi) = U(\phi)\, H_0(x)\, U^*(\phi), \tag{11}$$

then, clearly $\partial_\phi Tr(PH)(x,0) = 0$. [1]

Eq. (3) generalizes to the case where x is multidimensional. In the applications we consider x is two dimensional and naturally represented as $x \in \mathbb{C}$. Assuming no persistent response, the adiabatic transport is:

$$\begin{aligned} Tr\Big(\rho\, \partial_\phi H\Big) &= \frac{\hbar}{\tau}\, Re\left\{Tr\Big(\Omega_{\phi x}(P)\Big)\dot{x}\right\} + O\left(\frac{1}{\varepsilon\tau}\right) \\ &= \hbar\, Re\, \left\{Tr\Big(\Omega_{\phi x}(P)\Big)\, \frac{dx}{dt}\right\} + O\left(\frac{1}{\varepsilon\tau}\right). \end{aligned} \tag{12}$$

In a molecular ring the current observable is

$$I = -c\, \frac{\partial H}{\partial \phi}, \tag{13}$$

where ϕ is the flux threading the ring in Gaussian units. It follows that the charge Q transported in a cycle in x space, in the adiabatic limit, with $H(x,0)$ time reversal invariant, is:

$$\begin{aligned} Q &= -c \oint dt\, Tr\Big(\rho\, \partial_\phi H\Big) = -\hbar c\, Re \oint Tr\Big(\Omega_{\phi x}(P)\Big)dx \\ &= -e\Phi_0\, Re \oint Tr\Big(\Omega_{\phi x}(P)\Big)dx. \end{aligned} \tag{14}$$

$\Phi_0 = \frac{\hbar c}{e}$ is the quantum of flux. Note that in atomic units where $e = \hbar = 1,\ c = 137$, the unit of quantum flux is a large number. This will be important subsequently, as we shall see. Eq. (14) will be our basic tool. Note that the factors in front of the adiabatic curvature must be as they are on dimensional grounds.

3 Sheared Hückel Models

In the Hamiltonians we consider, $H(x,\phi)$, x denotes a deformation and ϕ magnetic flux. The magnetic flux is virtual and is only used to define the current operator. The family $H(x,0)$ is time reversal invariant.

[1] This mechanism is responsible for the absence of persistent currents in infinite chains irrespective of the question whether time reversal is broken or not.

By Wigner von-Neumann theorem, level crossings for time reversal invariant Hamiltonians are of codimension two. That is, like a point in a plane or a line in three space. For a cycle of deformation to pinch a point of level crossings, x space must be at least two dimensional. The simplest case is when x space is precisely two dimensional.

The space of deformation of a molecule with N nuclei is $3(N-2)$ dimensional [2]. A two dimensional subspace we shall focus on is the space of uniform shears in a plane.

The generators of uniform shears in two dimensions are the 2×2 matrices g_1 and g_2 of Eq. (1). Uniform shears can be represented by vectors $\vec{x}$ in $\mathbb{R}^2$, so that the shear associated to $\vec{x}$ is represented by the linear map $1+x_1g_1+x_2g_2$. It is convenient to use complex notation so $\vec{x}$ is represented by a complex number, $x \in \mathbb{C}$. Under the shear x a point d in the sheared plane is transformed to

$$d \to d + x\bar{d}.$$

The correspondence between the vector and complex representation is:

$$\vec{x} \to x = x_1 + ix_2, \quad \vec{d} \to d = d_1 + id_2, \quad g_1\vec{d} \to \bar{d}, \quad g_2\vec{d} \to i\,\bar{d}.$$

The length of d is stretched according to:

$$|d|^2 \to |d + x\bar{d}|^2 \;\; = \;\; |d|^2 + x\bar{d}^2 + \bar{x}d^2 + |x|^2|d|^2. \tag{15}$$

Suppose, for simplicity, that the hopping amplitude h_{ij} between sites i and j of a planar molecule is a function (typically, an exponential) of the distance $|d_{ij}|^2$ between the sites: $h_{ij} = h(|d_{ij}|^2)$. Under a small uniform deformation the hopping amplitudes will transform (to linear order) according to

$$h(|d|^2) \to h(|d|^2) + 2\,h'(|d|^2)\,Re\,(x\bar{d}^2).$$

In particular, the Hückel model of such a molecule is, to linear order, of the form

$$H(x) = H_0 + x\,(\partial_x H) + \bar{x}\,(\partial_{\bar{x}} H), \tag{16}$$

where H_0, $(\partial_x H)$ and $(\partial_{\bar{x}} H)$ are $N \times N$ matrices.

As an example consider the Hückel model associated with the sheared planar molecular necklace X_p of p sites. The tight binding model of such a necklace, see Fig. 2, is

$$H(\{h\}) = \begin{pmatrix} 0 & h(|d_1|^2) & 0 & . & 0 & h(|d_p|^2) \\ h(|d_1|^2) & 0 & h(|d_2|^2) & . & . & 0 \\ 0 & h(|d_2|^2) & 0 & . & . & . \\ . & . & . & . & . & 0 \\ 0 & . & . & . & 0 & h(|d_{p-1}|^2) \\ h(|d_p|^2) & 0 & . & 0 & h(|d_{p-1}|^2) & 0 \end{pmatrix}. \tag{17}$$

[2] The $3N$ nuclear coordinates include 3 center of mass coordinates and 3 Euler angles that do not correspond to deformations.

We fix the length scale so that the unstrained molecule has p equidistant atoms on a circle of perimeter p. The d_j bond in the unstrained necklace is a complex number of modulus one:

$$d_j = \frac{\omega^j - \omega^{j-1}}{|\omega - 1|} = i\omega^{j-1/2},$$

with $\omega = \exp(i\theta)$, $\theta = 2\pi/p$ and $j = 1 \dots p$. A shear x changes the distances by

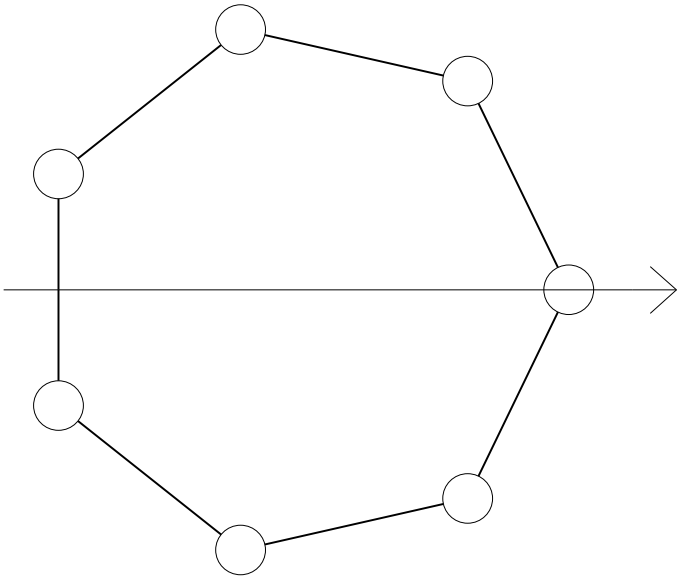

Figure 2: Molecular necklace

$$Re\,(\bar{d}_j^2 x) = -Re\,(\omega^{2j-1}\bar{x}). \tag{18}$$

This gives the two parameter family of Hamiltonians $H(x, \bar{x})$. In particular

$$H_0 = h(1)\begin{pmatrix} 0 & 1 & 0 & . & 1 \\ 1 & 0 & 1 & . & 0 \\ 0 & 1 & 0 & . & 0 \\ . & . & . & . & . \\ 0 & . & . & 0 & 1 \\ 1 & . & . & 1 & 0 \end{pmatrix},\ \partial_{\bar{x}} H = -h'(1)\begin{pmatrix} 0 & \omega & 0 & . & \omega^{-1} \\ \omega & 0 & \omega^3 & . & 0 \\ 0 & \omega^3 & 0 & . & 0 \\ . & . & . & . & . \\ 0 & . & . & 0 & \omega^{-3} \\ \omega^{-1} & . & 0 & \omega^{-3} & 0 \end{pmatrix}. \tag{19}$$

4 Adiabatic Curvature Near Crossing

The adiabatic curvature near conic crossing was studied in [Berry 1984] in the isotropic situation and by [Simon 1983] in the general case. The Hückel model of sheared molecular rings turns out to give an intermediate situation. In addition

it also leads to certain non-conic crossings. We therefore explore this situation in some detail.

Any two level system can be described as

$$H_{1/2}(x,\phi) = \bar{n}\sigma_+ + n\,\sigma_- + n_3\,\sigma_3, \tag{20}$$

where our convention for Pauli matrices is:

$$\sigma_+ = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \quad \sigma_- = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}.$$

A formula for the leading behavior of the $x\phi$ component of the adiabatic curvature is:

Proposition 4.1 *Let $H(x,\phi)$ be a Hermitian 2×2 matrix as in Eq. (20), with $x\in\mathbb{C}$ and $\phi\in\mathbb{R}$, such that to leading order in x and ϕ (as $x,\phi\to 0$)*

$$n \approx g x^m,\ n_3 \approx f\phi, \quad f\in\mathbb{R},\ g\in\mathbb{C}. \tag{21}$$

Then to leading order

$$Tr\,\Omega_{x\phi} \approx \pm\frac{m\,f|g|^2|x|^{2m-2}\bar{x}}{4i|\vec{n}|^3}, \quad 2\vec{n} = (n+\bar{n}, -i(n-\bar{n}), 2n_3) \tag{22}$$

Proof: A result of [Berry 1984] is that the curvature is half the spherical angle. In complex notation it reads:

$$\begin{aligned} Tr\,\mathbf{\Omega} &= \pm\frac{1}{2|\vec{n}|^3}\ \vec{n}\cdot d\vec{n}\times d\vec{n} \\ &= \pm\frac{\bar{n}\,dn - n\,d\bar{n}}{4i\,|\vec{n}|^3}\wedge dn_3. \end{aligned} \tag{23}$$

It follows that for a *circle* of deformation, $|x| = const$, the contribution of the adiabatic curvature to the charge transport, in the limit $x\to 0$, is:

$$Q_\pm \approx \pm\, e\Phi_0\, m\pi\ f|g|^2\,\frac{|x|^{2m}}{|\vec{n}|^3} \approx \pm\, e\Phi_0 m\pi\ \begin{cases} \frac{f}{|gx^m|} & \phi = 0; \\ \frac{|g|^2}{f^2}\,\frac{|x|^{2m}}{\phi^3} & \phi\neq 0. \end{cases} \tag{24}$$

Q diverges as $|x|\to 0$ if, and only if, $\phi = 0$. If $\phi\neq 0$, then Q reaches the maximum value $2m\pi e\Phi_0/(3^{3/2}\phi)$ for $|gx^m| = \sqrt{2}f\phi$ and vanishes in the limit.

5 Trimers

The smallest molecular ring is a trimer X_3. H_3 and Na_3 are examples. The case of a trimer is special in that the space of internal coordinates is three dimensional (since

a triangle is uniquely determined by its sides). Three is also the dimension of linear transformations of the plane: Two shears and one dilation.

A canonical choice for the internal coordinates of trimers goes back to Jacobi [Mead 1992, Mead and Truhlar 1979]. It is instructive to relate these with the coordinates associated with uniform shears. We start by reviewing the Jacobi coordinates [Mead 1992].

Let $\vec{a},\ \vec{b},\ \vec{c}$ be the distances between the 2-3, 3-1 and 1-2 nuclei so that $\vec{a}+\vec{b}+\vec{c}=0$. The Jacobi coordinates are

$$\vec{u}=\sqrt{\frac{3}{2}}\,\vec{a},\quad \vec{v}=\sqrt{\frac{1}{2}}\,(\vec{b}-\vec{c}). \tag{25}$$

Equivalently:

$$\vec{a}=\sqrt{\frac{2}{3}}\,\vec{u},\quad \vec{b}=\sqrt{\frac{1}{2}}\,\vec{v}-\sqrt{\frac{1}{6}}\,\vec{u},\quad \vec{c}=-\sqrt{\frac{1}{2}}\,\vec{v}-\sqrt{\frac{1}{6}}\,\vec{u}. \tag{26}$$

Evidently, when $\vec{u}$ and $\vec{v}$ are parallel the trimer is a linear molecule. The scale and shape of the trimer are determined by the three coordinates:

$$\begin{aligned} q=\vec{u}^2+\vec{v}^2 &= \vec{a}^2+\vec{b}^2+\vec{c}^2,\\ qX=2\,\vec{u}\cdot\vec{v},\quad qY &= \vec{u}^2-\vec{v}^2. \end{aligned} \tag{27}$$

Since $|X|,|Y|\le 1$ one can, without loss, set

$$X=\sin\theta\,\cos\varphi,\quad Y=\sin\theta\,\sin\varphi,\quad \theta\in[0,\pi/2],\ \varphi\in[0,2\pi). \tag{28}$$

The shape is determined by X and Y alone. This can be seen by considering the lengths (squared) of the sides:

$$\begin{aligned} a^2 &= \frac{q}{3}\,(1+X)\,,\quad b^2=\frac{q}{3}\left(1-\frac{1}{2}\,X-\sqrt{\frac{3}{4}}\,Y\right),\\ c^2 &= \frac{q}{3}\left(1-\frac{1}{2}\,X+\sqrt{\frac{3}{4}}\,Y\right). \end{aligned} \tag{29}$$

Thinking of θ and φ as the canonical spherical angles, we see that the equilateral triangle sits at the north pole. The equator corresponds to degenerate triangles where the trimer is linear. The locus of isoceles triangles are the three meridians

$$\tan\varphi=0,\quad \tan\varphi=\pm\sqrt{3}. \tag{30}$$

And finally, $\varphi\to\pi-\varphi$ reverses orientation. This completes the description of the Jacobi coordinates.

The area (squared) of the triangle is proportional to

$$4\,|\vec{u}\wedge\vec{v}|^2=q^2\,(1-Y^2-X^2). \tag{31}$$

We are interested on triangles which are almost equilateral, that is, near the north pole. To linear order in X and Y, constant area is the same as constant q. Comparing Eq. (29) and Eq. (15) we see that, within this linear regime, an almost equilateral triangle with given coordinates X and Y is obtained by applying a shear to an equilateral triangle, where the complex x defined in section 3 is $x = \frac{X}{2} + i\frac{Y}{2}$. For this identification we have taken an equilateral triangle oriented so that $\vec{a}$ is parallel to the real axis of the complex plane; rotation of the equilateral triangle by $\varphi_0/2$ in the complex plane amounts to multiplication of x by a constant phase $e^{-i\varphi_0}$.

Consider now the molecular trimer X_3 threaded by a fictitious flux, so that the Hückel model [3] becomes

$$H(a,b,c,\phi) = \begin{pmatrix} 0 & a & \bar{\xi}c \\ a & 0 & b \\ \xi c & b & 0 \end{pmatrix}, \tag{32}$$

where, with abuse of notation, a, b, c are shorthand for $h(\vec{a}^2), h(\vec{b}^2), h(\vec{c}^2)$. The virtual flux is

$$\xi = \exp 2\pi i \left(\frac{\phi}{\Phi_0}\right). \tag{33}$$

We chose a gauge so that the flux is associated with the c-bond.

Since the characteristic equation for $H(a,b,c,\phi)$ is

$$-E^3 + E(a^2+b^2+c^2) + 2abc\cos 2\pi\left(\frac{\phi}{\Phi_0}\right) = 0,$$

eigenvalues crossing occurs at

$$\pm(a^2+b^2+c^2)^{3/2} + 3^{3/2}abc\cos 2\pi\left(\frac{\phi}{\Phi_0}\right) = 0.$$

Since the geometric mean is always less than the arithmetic mean:

$$(a^2+b^2+c^2)^{3/2} \geq 3^{3/2}abc,$$

crossing can only occur if the flux is an integer or half an integer: $\xi = \pm 1$. Moreover since the geometric and arithmetic mean coincide only if all the elements are identical, the locus of crossings is $|a| = |b| = |c|$ and $\xi = \pm 1$. The simple eigenvalue is $2a$ (the top state if a is positive) and the corresponding eigenvector is $|1\rangle = \frac{1}{\sqrt{3}}(1,1,1)$. (Recall that $\xi = 1$). The degenerate eigenvalue is $-a$ and is two fold degenerate.

We consider now a small cycle of deformations which pinches the line of level crossing, see fig. 3. Such a cycle is

[3] The model is naturally associated with three (π) electrons molecule, e.g. H_3 molecule. If the electrons are non interacting, and spin degeneracy is taken into account, then the ground state is fully occupied by the two electrons and the first excited state occupied by one electron. The charge transported (to leading order in x) is the same as the charge transported by a single electron in the ground state. The currents of the two other electrons mutually cancel.

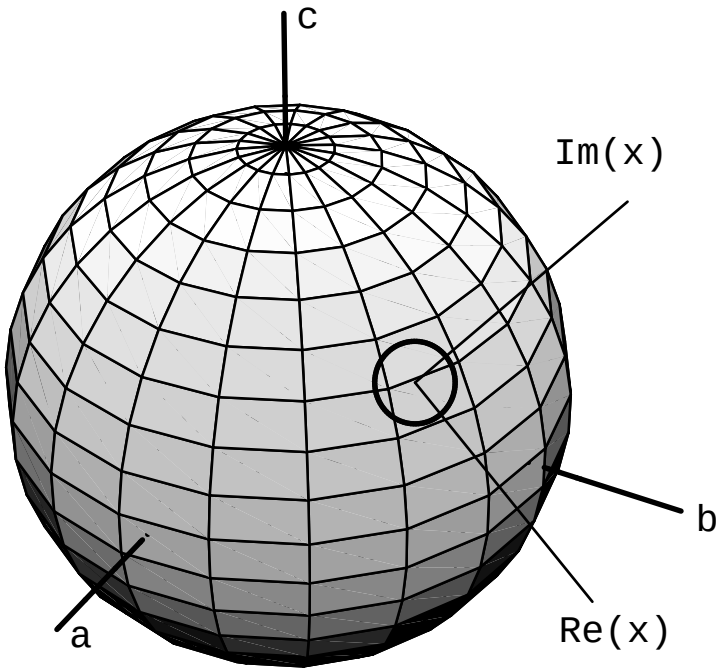

Figure 3: A cycle of deformation

$$\begin{aligned} a(x) &= h(1) + h'(1)(\omega\bar{x} + \bar{\omega}x); \\ b(x) &= h(1) + h'(1)(\bar{x} + x); \\ c(x) &= h(1) + h'(1)(\overline{\omega x} + \omega x), \end{aligned} \tag{34}$$

where ω is a cube root of unity and $x \in \mathbb{C}$ runs on a small circle in the complex plane surrounding the origin. The phase of x has been chosen as in section 3.

We are interested in the amount of charge moving around the triangle when the molecule undergoes this cycle of deformations that encircles the line of gap closures. In the case of a single electron, this charge can be interpreted as the total number of turns around the molecule that the electron makes.

The expansion of the Hamiltonian near zero flux and near the equilateral triangle takes the form :

$$H(x, \phi) = H_0 + h'(1)\,(x\,V_x + \overline{x\,V_x}) + 2\pi\,h(1)\left(\frac{\phi}{\Phi_0}\right)\,V_\phi, \tag{35}$$

where

$$V_x = \begin{pmatrix} 0 & \bar{\omega} & \omega \\ \bar{\omega} & 0 & 1 \\ \omega & 1 & 0 \end{pmatrix} \quad ; \qquad V_\phi = i \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}.$$

The degeneracy splits in first order of perturbation theory, both in ϕ and in x. The local behavior near crossing is given by the 2×2 matrix as in Eq. (20) with

$$f = \frac{2\pi h(1)}{\Phi_0\sqrt{3}}, \quad g = 2\bar{\omega}h'(1), \quad m = 1. \tag{36}$$

For a circular orbit, $|x| = const.$, the total charges transported per cycle in the almost crossing state is given by Eq. (24). If there is no external magnetic field, so the flux $\phi = 0$, one finds:

$$Q = \pm\, e \left(\frac{\pi^2}{\sqrt{3}}\right) \left(\frac{h(1)}{h'(1)}\right) \frac{1}{|x|}. \tag{37}$$

The divergence of the charge transport near conic crossing is universal for conic crossing. It describes the remarkable fact that the smaller the cycle that pinches the degeneracy, the more charge it transports. The overall constant is inversely proportional to the logarithmic derivative of the hopping amplitude.

The current is *not* large. Only the ratio of current to the rate of driving is large. As the circle is shrunk, the rate of driving must also decrease in order for the adiabatic theory to apply.

Driving a system by an infinitesimal cycle that pinches a crossing may or may not be an easy thing to do. In molecular rings, X_p, this may well be a difficult thing to accomplish, since the Jahn Teller instability fixes a pinching cycle, or finite radius, which is the ground state manifold of the molecule. This point is discussed in more detail in the last section.

6 Sheared Molecular Necklaces

The study of charge transport in necklaces of p atoms with zero threading flux requires analysis of the gap closures for $\xi = 1$. We take the Hamiltonian (19), with flux dependence given by the obvious generalization of (32). The eigenvalues of the unstrained molecule are:

$$E_m = 2\cos(m\theta), \quad m = 0, \ldots, \frac{p-1}{2}, \quad \theta = \frac{2\pi}{p}.$$

For simplicity, we deal here only with the case that p is odd. Note that the energies are in decreasing order, fig 4. All energies, except $m = 0$ are doubly degenerate so that the projection on the m-th subspace is spanned by $|\pm m\rangle$ where

$$|m\rangle = \frac{1}{\sqrt{p}} \begin{pmatrix} \omega^m \\ \omega^{2m} \\ \omega^{3m} \\ \cdots \\ 1 \end{pmatrix}, \quad m = 0, \pm 1, \ldots, \pm\frac{p-1}{2}.$$

One finds

$$\sqrt{p}\,(\partial_{\bar{x}} H)|m\rangle = -h'(1)(\bar{\omega}^{m+1} + \omega^{m+1}) \begin{pmatrix} \omega^m \\ \omega^{2m+2} \\ \omega^{3m+4} \\ .... \\ \omega^{-2} \end{pmatrix}; \quad \sqrt{p}\,(\partial_\phi H)|m\rangle = \frac{2\pi i h(1)}{\Phi_0} \begin{pmatrix} -1 \\ 0 \\ .... \\ 0 \\ \omega^m \end{pmatrix}.$$

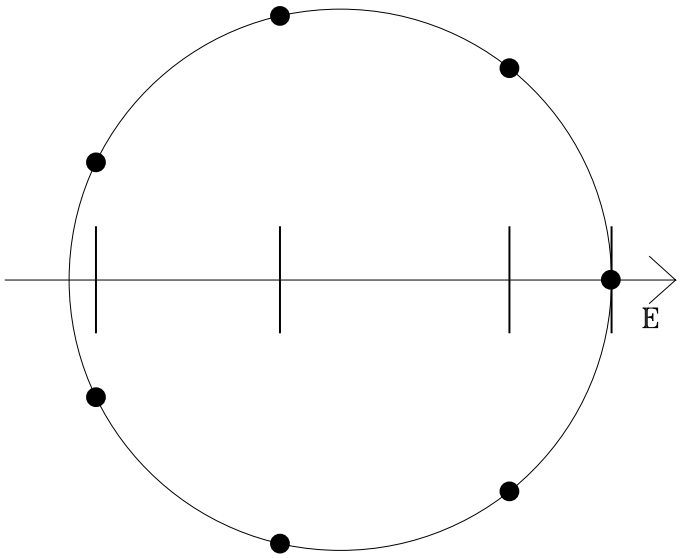

Figure 4: Eigenvalues and the roots of unity

$\partial_{\bar{x}} H$ is a double right shift:

$$\begin{aligned}\langle m|\partial_{\bar{x}} H|m+k\rangle &= -h'(1)\,\frac{\bar{\omega}^{m+k+1}+\omega^{m+k+1}}{p}\,(\omega^k+\omega^{2k+2}+\omega^{3k+4}+\ldots)\\ &= -h'(1)\,\delta(k+2)\,\bar{\omega}^2\,(\bar{\omega}^{m-1}+\omega^{m-1}).\end{aligned} \tag{38}$$

Similarly,

$$\langle m|\partial_\phi H|k\rangle = 2\pi i h(1)\,\frac{\omega^k-\bar{\omega}^m}{p\Phi_0} = -\frac{4\pi h(1)}{p\Phi_0}\,\omega^{\frac{k-m}{2}}\,\sin(\frac{k+m}{2}\theta)$$

The two dimensional subspace associated with $|\pm m\rangle$, for $m=1,\ldots,\frac{p-1}{2}$, is split in first order of perturbation theory in the ϕ variable. In contrast, the split is in order m of perturbation theory in the x variable. All we need to compute is the 2×2 matrix describing the crossing, and in the case $\xi=1$, see fig 5, we find (up to an overall scale):

$$\begin{aligned}H_{1/2} = \;& 2(-h'(1))^m\;\left(\prod_{k=1}^{m-1}\frac{\cos(-m+2k-1)\theta}{\cos m\theta-\cos(m-2k)\theta}\right)\cos(m-1)\theta\;\left(\overline{(\omega^2 x)}^m\sigma_+ + (\omega^2 x)^m\sigma_-\right)\\ &- \quad\frac{4\pi h(1)}{p\Phi_0}\,\sin(m\theta)\,\sigma_3\,\phi.\end{aligned} \tag{39}$$

This puts us in the framework of proposition 4.1 with explicit values for g, m and f. Note that as far as degenerate perturbation theory is concerned, there are also other terms that split the degeneracy, like $x\phi$. However all these are irrelevant for

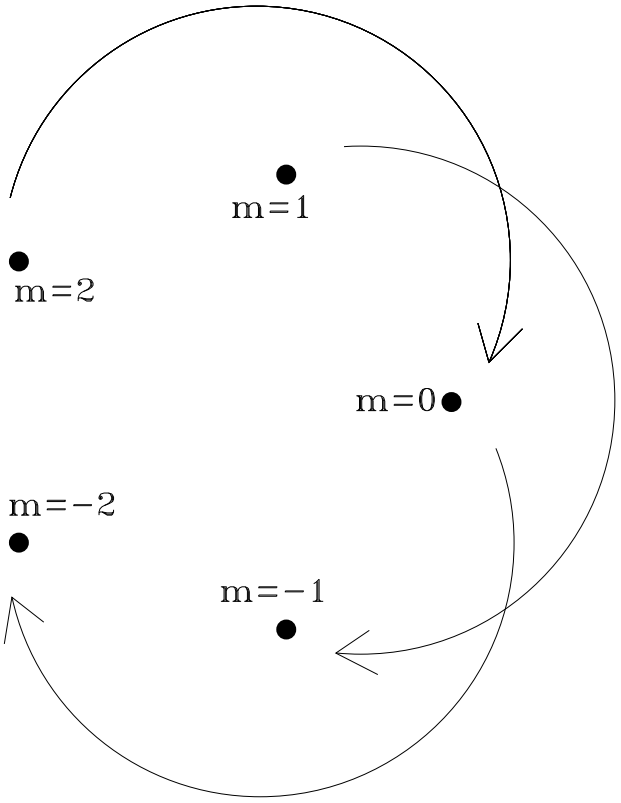

Figure 5: Coupling of states by the perturbation

computing curvature since g, m and f are all we need in Eq. (22). The transport is given by Eq (24).

We want to conclude this section with two cautionary remarks about the scope of validity of the results of this section. The moral of both of these is that the results for conic crossings have a wider scope of validity than the results for non-conic crossings.

1. The theory of deformed tight binding Hamiltonians was developed to first order in x. For gaps that open to first order, that is for conic crossings, such a perturbation expansion is consistent. However, for gaps that open in higher orders, one should have considered sheared tight binding models valid to higher orders in x. To lowest order, Eq. (39) may or may not remain applicable, depending on whether there exist paths that connect $|m\rangle$ to $|-m\rangle$ more efficiently than in Fig. 5.

2. We have restricted the space of deformations to uniform shears. When other deformations are also possible, as is the case for planar molecules X_p with $p \geq 4$, these cannot be neglected: it is always possible to build a deformation that will open the gap in first order and will therefore provide the lowest order perturbation.

7 Crossing Bands and Direct Integrals

In this section we describe a version of the equation for adiabatic transport, Eq (3), for systems described by direct integrals. This is the case for infinite periodic chains of non-interacting electrons that admit Bloch decomposition [Grossmann 1972]. From a physical point of view there are two important consequences to this extra structure. The first is that charge transport becomes integral. The second, and related, is that the formulas for charge transport, which for finite molecular rings involved non-universal factors (the logarithmic derivative of the hopping amplitudes), become truly universal. Studies of Chern numbers in the context of charge transport have been made in [Bellissard, Bovier and Ghez 1991, Kunz 1993, Thouless 1983, Kreft and Seiler 1996, Novikov 1981, Poilblanc et al. 1991, Tan 1994, Wilkinson 1984, Yakovenko 1991].

Consider the Hamiltonian represented by a direct integral (over the torus):

$$H_B(x) = \int_{\oplus} H(x,\phi)\,\frac{d\phi}{2\pi}.$$

$H(x,\phi)$ acts on a fixed Hilbert space, say $\mathcal{H}$. In this and the following section ϕ will stand for Bloch momentum. A spectral projection on an energy band is

$$P_B(x) = \int_{\oplus} P(x,\phi)\,\frac{d\phi}{2\pi}.$$

$P(x,\phi)$, the spectral projection for $H(x,\phi)$, is smooth and periodic in ϕ. Consider the observable

$$\Big(\partial_\phi H_B\Big)(x) = \int_{\oplus} \partial_\phi H(x,\phi)\,\frac{d\phi}{2\pi}.$$

This is interpreted as current: It is made up from velocity $\partial_\phi H(x,\phi)$ and density $\frac{d\phi}{2\pi}$. In this case, ϕ runs on the unit circle. The persistent response for infinitely many non interacting fermions filling the band vanishes by periodicity:

$$Tr\left(P_B\partial_\phi H_B\right) = \int_{-\pi}^{\pi} \frac{d\phi}{2\pi}\,\partial_\phi\, Tr\,(PH) = 0. \tag{40}$$

Nearly Crossing Bands: The question we address is what can one say about "axial" integrals of the adiabatic curvature

$$\int_{-\pi}^{\pi} \frac{d\phi}{2\pi} Tr\,\Omega_{\phi x}\Big(P(x,\phi)\Big) = -i\int_{-\pi}^{\pi} \frac{d\phi}{2\pi}\,Tr\left(P(x,\phi)\,[\partial_\phi P(x,\phi), \partial_x P(x,\phi)]\right), \tag{41}$$

in the case of nearly crossing bands. More precisely, suppose that $x = 0$ is a band closure for some value of ϕ. What is the analog of Eq. (24) in this case?

Suppose that $P(x,\phi)$ is a projection in $\mathbb{C}^2$ associated with the two level Hamiltonian Eq. (20), with $n(x,\phi)$ and $n_3(x,\bar{x},\phi)$ as in proposition 4.1 and we set the origin of ϕ space at the zero of n and n_3, assuming approach to zero as in Eq. (21).

In general, there may be several such zero points. The contributions of these behave additively and it is therefore enough to consider one. Since the $d\phi$ integral is dominated by the singularity:

$$\begin{aligned}\int_{-\pi}^{\pi}\frac{d\phi}{2\pi}\,Tr\,\Omega_{\phi x}\Big(P(x,\phi)\Big) &= \pm\int_{-\pi}^{\pi}\frac{f}{4i\,(|n|^2+n_3^2)^{3/2}}\bar{n}\frac{\partial n}{\partial x}\frac{d\phi}{2\pi}\\ &= \pm\frac{m|g|^2}{8\pi i}|x|^{2m-2}\bar{x}\int_{-\infty}^{\infty}\frac{f\,d\phi}{(|gx^m|^2+|f\,\phi|^2)^{3/2}}+O(1)\\ &= \pm\frac{m}{8\pi i|x|^2}\bar{x}\int_{-\infty}^{\infty}\frac{d\phi}{(1+\phi^2)^{3/2}}+O(1)\\ &= \pm\frac{m}{4\pi i x}+O(1).\end{aligned}\tag{42}$$

A similar formula holds for $\Omega_{\phi\bar{x}}(P)$. Now the divergence is like x^{-1} and the power is independent of the order of crossing. The order shows up as a linear factor.

In the case that there are several such points the adiabatic response collects the contribution from all of them. These come with one sign for the top gap closure and the opposite sign for the bottom gap closure, fig. 6.

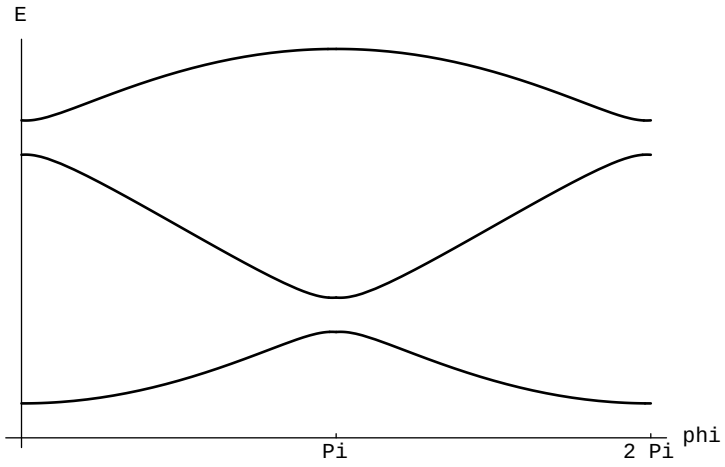

Figure 6: Top and bottom gap closures

For fixed Fermi energy in a gap, with one point of gap closure, the total charge transport by a loop[4] encircling a gap closure, is precisely :

$$Q = \mp m.\tag{43}$$

Homeopathy means that integral charge is transported even if the deformation is minuscule.

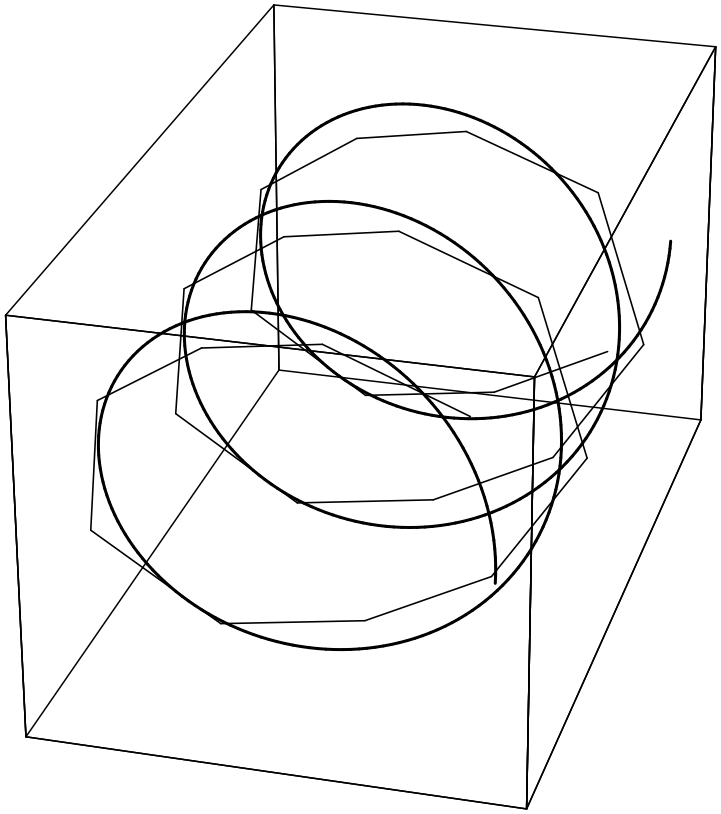

Figure 7: Shearing a helix in the transverse plane

8 Homeopathic Charge Pump

Consider an infinitely long helical chain: A single pitch of the helix is made of an open circle with p atoms per pitch. The cross section of the helix is a circle and the unstrained atoms on the circle are equidistributed. Of course, there is no reason in the world why a chain of identical atoms would want to form a helix. So we may imagine that this structure is enforced by an external constraint. We shall consider uniform shears of the helix in a plane perpendicular to the axis of the helix.

A tight binding model of such a helix is described by a $p \times p$ matrix $H(x, \phi)$, where $x \in \mathbb{C}$ is the deformation and $x = 0$ is the undeformed helix. ϕ stands for the Bloch momentum, traditionally denoted by k. $H(x, \phi)$ is identical to the tight binding (Hückel) Hamiltonian of a necklace of p atoms enclosing a flux ϕ. Such Hamiltonians were analyzed in section 6.

Consider a quantum system of infinitely many (non interacting, spinless) electrons on such a helix so that there are q electrons per p atoms. The unstrained chain, $x = 0$, has continuous spectrum in the interval $[-2, 2]$ without any gaps. It is convenient to think of this as a collection of p bands with closed gaps:

$$[-2, 2\cos(\pi(1-1/p))],\ [2\cos(\pi(1-1/p)), 2\cos(\pi(1-2/p))],\ \ldots [2\cos(\pi/p), 2].$$

[4]Not necessarily a circle.

Shearing the chain in the plane perpendicular to the chain axis, see fig. 7, will break the spectrum into p bands, so that the lowest q bands will be occupied. Consider now a cycle of deformations $|x| = \varepsilon$ which avoids the origin. Such a cycle pinches the gap closure at $x = 0$. (See section 3.) Collecting results from the sections below gives the following result:

A small cycle of shears in the plane perpendicular to the axis of an infinite helix, with pitch p (p odd), transports integer (non zero) charges from $-\infty$ to ∞ even if the orbit is arbitrarily small (but not zero). The amount of transported charge is $q/2$ if q, the number of electrons per pitch of the helix, is even. If q is odd, then the charge transport is $-(p-q)/2$.

These results can be seen as follows. By Floquet theory, the band edges are determined by $H(x, 0)$ and $H(x, \pi)$. The two cases are simply related when p is odd since the Hamiltonian, Eq. (17), satisfies

$$H(\{h\}, 0)U = -UH(\{h\}, \pi), \tag{44}$$

with a fixed unitary

$$U_{ij} = (-)^j \, \delta_{ij}.$$

Using this, the spectral and geometric results for the zero flux of section 6 can be easily translated to the $\phi = \pi$ case.

The lowest gap near $2\cos(\theta(p-1)/2)$ opens in $(p-1)/2$-th order of degenerate perturbation theory. By symmetry, Eq. (44), this then also holds for the top gap. The second gap from the bottom opens, likewise, as the second gap from the top. This opens in first order of degenerate perturbation theory, etc. This is explained in fig. 5. The general rule which gives the order in which a gap opens depends on the parity of the gap. The results are summarized in a table that also gives the Chern number of the gap:

Gap	Order	Chern
2j	j	j
2j+1	$\frac{p-1}{2} - j$	$-\frac{p-1}{2} + j$

9 Elastic and Magnetic Jahn Teller Instabilities

The analysis carried out so far assumed that the deformation x and the flux ϕ are externally controlled parameters which can be varied at will. In reality, both are dynamic variables with their own equations of motion. The question one needs to consider is how this may affect transport.

For example, in our analysis it is important that time reversal is not spontaneously broken and the flux ϕ was a virtual flux. The dynamical equations could, in principle, force $\phi \neq 0$. If this was to happen then homeopathic response is censored.

Even for a molecular trimer X_3 (in three dimensions), the full dynamics is a formidable problem which brings out all the intricacies of the three body problem [Mead 1992, Mead and Truhlar 1979, Englman 1972, Bersuker 1984]. Similarly, the full dynamics of ϕ is determined by QED.

The static problem is much simpler. It is determined by an energy functional whose minimizers are classical equilibrium configurations. For the nuclear coordinates the minimizer gives the ground state configurations and for the flux it gives Ampère's law. Such a functional is :

$$E(x,\phi) + Q(x) + \frac{1}{2L}\phi^2. \tag{45}$$

Here $E(x,\phi) = E(x,\phi+\Phi_0)$ is an eigenvalue of say the Hückel Hamiltonian, $Q(x)$ is a classical potential energy and L is a geometric constant (L/c^2 is the self-inductance of the molecule). Note that the period of $E(x,\phi)$ in ϕ is large since in atomic units $\Phi_0 = c = 137$ is large.

The minimizer of this functional with respect to the flux gives the analog of Ampere's equation (in Gaussian units)

$$0 = \frac{\partial E(x,\phi)}{\partial \phi} + \frac{\phi}{L} = -\frac{1}{c}\, I + \frac{\phi}{L}. \tag{46}$$

Let us now specialize to the case of planar molecular rings X_p and let us assume that the elastic energy $Q(x)$ depends only on the distances $|d_j|$ between neighboring atoms. From Eq. (18) the elastic energy of a molecular necklace X_p, in the Harmonic approximation, is an isotropic function of x:

$$\begin{aligned} Q(x) &= \frac{K}{2}\sum(|d_j(x)| - |d_j(0)|)^2 = \frac{K}{8}\sum(\omega^{2j-1}\bar{x} + \bar{\omega}^{2j-1}x)^2 \\ &= \frac{pK}{4}|x|^2, \end{aligned} \tag{47}$$

where K is the "spring constant". From Eq. (39), the electronic energy surface of the one-electron state near crossing is also isotropic in x, and the energy functional is of the form:

$$\pm\sqrt{|g|^2|x|^{2m} + (f\phi)^2} + \frac{pK}{4}|x|^2 + \frac{1}{2L}\phi^2. \tag{48}$$

In this functional g, K, L are all of order one but f is a small number of order $1/\Phi_0$.

It is convenient to use rescaled variables

$$y = x^m, \quad \varphi = \phi/\Phi_0. \tag{49}$$

In these variables the energy functional is

$$\pm\sqrt{|g|^2|y|^2 + (f\Phi_0)\varphi^2} + \frac{pK}{4}|y|^{2/m} + \frac{\Phi_0^2}{2L}\varphi^2. \tag{50}$$

Here g, K, L and $f\Phi_0$ are all of order one in atomic units, while $\Phi_0 = 137$.

The minimizers of this functional are as follows:

1. With the positive sign for the square root the minimizer is the trivial solution $\phi = \varphi = y = x = 0$.

2. With the negative sign for the square root and conic crossing, $m = 1$, the minimizer has $\phi = \varphi = 0$ and $|x| = \frac{2|g|}{pK} = \frac{4|h'(1)|}{pK}$. $\varphi = 0$ because its "spring constant" is stiff, of order 10^4. This solution is the classical Jahn Teller instability. Because the energy functional is isotropic, the minimizer is a circle. The charge transported in this cycle is

$$Q = \pm \frac{\pi^2 eKh(1)\sin(2\pi/p)}{2\left[h'(1)\right]^2}\,. \tag{51}$$

3. With the negative sign for the square root and non-conic crossing, $m \geq 2$, the stiff term in (50) is now the elastic spring, which is not harmonic. Therefore the minimizer is $x = 0$ and $|\phi| = L|f|$. This is a magnetic Jahn Teller instability, where there is spontaneous breaking of time reversal. Time reversal is only weakly broken because f is small: the spontaneous flux is of the order of $10^{-4}\Phi_0$. As we have already stressed in a previous section, conclusions drawn from sheared Hückel models in situations where the crossing is not conic, are fragile and depend sensitively on perturbations. This may be a reason why magnetic Jahn Teller has not been observed.

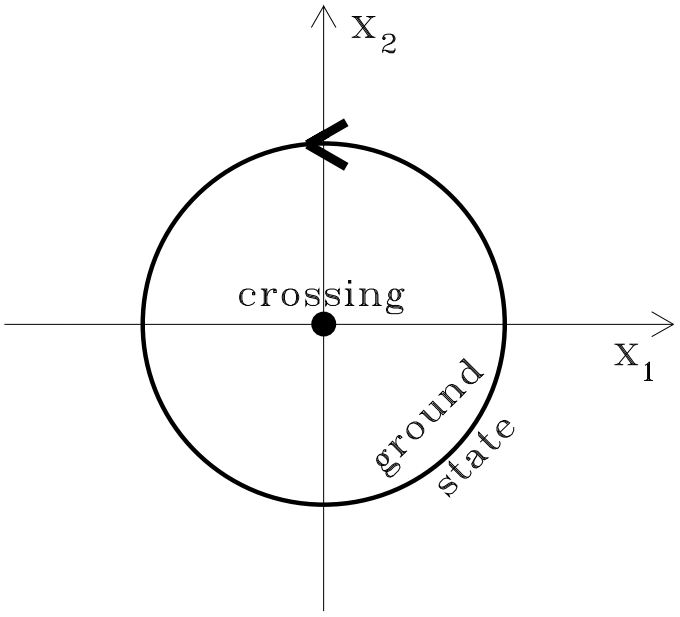

Figure 8: The preferred cycle of deformation.

Acknowledgments

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